On the Determination of Low Valency Titanium Compounds

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Synopsis

The methods for the determinations of bivalent, trivalent titanium, metallic aluminium and total amounts of aluminium and chlorine in the reaction products of titanium tetrachloride with metallic aluminium were studied. The amounts of bivalent and trivalent titanium were respectively determined by dissolving the sample in ferric sulfate solution and water, and then by titrating each solution with potassium permanganate or ferric solution. The total amount of aluminium was determined with oxine after the separation of titanium with sodium hydroxide, and chlorine was determined by the usual gravimetric method as silver chloride. The metallic aluminium content was estimated from the residue obtained by dissolving the sample in water, by gravimetric or volumetric method.

I. Introduction

In refining of metallic titanium, there is a step in which titanium tetrachloride is reduced with metallic aluminium powder to titanium trichloride and further to titanium dichloride. The low valency titanium compound contains titanium dichloride, titanium trichloride and metallic aluminium and probably some amounts of their oxides. In order to ascertain its composition, determination of bivalent and trivalent titanium, total titanium, metallic aluminium and total chlorine is required and examination of such determination methods were examined. Good results were obtained by the analytical procedures.

II. Experimental method

1. Dissolution of sample

The chloride compound to be used as a sample fumes in the air and is so easily oxidized that it is impossible to weight it directly with a chemical balance. The sample was therefore taken into a tared weighing bottle in approximately 1 g amount in carbon dioxide atmosphere, the whole was weighed, and by subtracting the weight of the bottle, the difference of the weights was considered as the sample taken. The weighing bottle containing the sample was placed in an Erlenmeyer flask dissolved in water or acids, and then the bottle was washed with water.

2. Determination of bivalent and trivalent titanium

The chloride of low valency titanium catches fire in the moist air and decomposes with fuming, is easily oxidized and is dissoluble in water, acids and alcohols, but is insoluble in ether. Pfordten[1] extracted only bivalent titanium

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(1) Pfordten, Liebig Ann. Chem., **237** (1887), 201.

with ether from the hydrochloric acid solution and called it the specific reaction; Patscheke and Schaller[2] extracted only trivalent titanium from quadrivalent titanium by the same method. This method, however, calls for too complicated procedures; bivalent titanium has a strong reducing action and generates hydrogen by decomposing water, when it dissolves in water, and its aqueous solution is extremely unstable, bivalent titanium being easily oxidized to trivalent titanium. Therefore, it is actually difficult, with this method, to make their separation and respective determinations.

On the other hand, trivalent titanium is comparatively stable in the air and is less hydrolyzable by water than quadrivalent titanium. Determination of trivalent titanium can be made simply even in the presence of quadrivalent titanium by titration with standard ferric solution in sulfuric or hydrochloric acid solution, using potassium thiocyanate as the indicator. The determination can also be made by titration of ferrous ion from the reaction $Fe^{3+}+Ti^{3+}\rightarrow Fe^{2+}+Ti^{4+}$, with standard potassium permanganate solution.

Determination of bivalent titanium is possible in the presence of trivalent titanium because bivalent titanium is oxidized to trivalent state by water and to quadrivalent titanium by ferric ion as in the case of trivalent titanium. Since the sample contains metallic aluminium, it is necessary to correct the titration value accordingly. The sample may contain a mixture of trivalent and quadrivalent titanium or bivalent and trivalent titanium, so the following procedures were adopted.

(i) Mixture of trivalent and quadrivalent titanium

Procedure A (Water dissolution method): The sample, 0.5~1 g, was placed in Erlenmeyer flask containing 100 ml of water and this was stirred in carbon dioxide atmosphere to effect complete solution. Insoluble metallic aluminium was collected by filtration with suction through a Gooch crucible with asbestos, and the residue and asbestos were washed thoroughly with water. The combined filtrate and washings were used as the sample. The filtrate was adjusted to about 1 N sulfuric acid concentration by the addition of 6 N sulfuric acid and was titrated with 0.1 N ferric ammonium sulfate solution using 10 ml of 40 per cent potassium thiocyanate solution as the indicator. The end point was a pale pink color which persists for 1 min and the amount of trivalent titanium was calculated from the following equation:

$$Ti^{3+}\% = \frac{\text{Titre of 0.1N } Fe(NH_4)(SO_4)_2 \times 0.479}{\text{Sample (g)}}$$

Procedure B (Ferric sulfate dissolution method): The sample, 0.5~1 g, was placed in an Erlenmeyer flask containing 3 g of ferric ammonium sulfate and 50 ml of 3 N sulfuric acid, dissolved with warming in carbon dioxide atmosphere and rapidly cooled with cold water. After cooling, ferrous ion formed by reduction with trivalent titanium and metallic aluminium was titrated with 0.1 N potassium permanganate solution. The end point was a pale pink color which persists for

(2) G. Patocheke and W. Schaller, Z. anorg. allgem. Chem., **235** (1938), 266.

1 min and this gave the titration value for the combined amount of trivalent titanium and metallic aluminium. Next, metallic aluminium was determined by either the gravimetric or volumetric method, and the titration value for ferrous ion was obtained by the amount of metallic aluminium, and the amount of trivalent titanium was calculated from the following equation:

$$Ti^{3+}\% = \frac{\text{Titre of 0.1N } KMnO_4 \text{ consumed by sample (ml)} - \text{Titre of 0.1N } KMnO_4 \text{ required for metallic Al (ml)}}{\text{Sample (g)}} \times 0.479$$

(ii) Mixture of bivalent and trivalent titanium

Procedure A′: The same procedure as the above B method was followed and the titre of 0.1N potassium permanganate required for ferrous ion formed by the oxidation of bivalent and trivalent titanium to quadrivalent titanium was obtained. Metallic aluminium was determined separately and the titre of 0.1N potassium permanganate for this amount was corrected. The corrected titre was designated A. Then the titre B, of 0.1N ferric ammonium sulfate solution required for the total titanium in this solution, was obtained and the amounts of bivalent and trivalent titanium were calculated by the following equations:

$$Ti^{2+}\% = \frac{[A(\text{ml}) - B(\text{ml})] \times 0.479}{\text{Sample (g)}}$$

$$Ti^{3+}\% = \frac{[B(\text{ml}) - (A(\text{ml}) - B(\text{ml}))] \times 0.479}{\text{Sample (g)}}$$

Procedure B′: With each sample, the titre D and C were obtained respectively by the method (i)A and (i)B, and the amounts of bivalent and trivalent titanium were calculated from the following equations:

$$Ti^{2+}\% = \left(\frac{C(\text{ml})}{\text{Sample A}'(\text{g})} - \frac{D(\text{ml})}{\text{Sample B}'(\text{g})}\right) \times 0.479$$

$$Ti^{3+}\% = \left[\frac{D(\text{ml})}{\text{Sample B}'(\text{g})} - \left(\frac{C(\text{ml})}{\text{Sample A}'(\text{g})} - \frac{D(\text{ml})}{\text{Sample B}'(\text{g})}\right)\right] \times 0.479$$

(The titre C is the corrected value with the amount required of 0.1N potassium permanganate solution for metallic aluminium.)

3. Determination of total titanium

Procedure: The sample, 0.5~1 g, was placed in a 300 ml beaker, 50 ml of 4N sulfuric acid was added, and dissolved by warming, or the sample was dissolved in a solution of sulfuric acid containing ferric ion, titrated with potassium permanganate, and this titrated solution was used. It was transferred to the amalgam reductor contained 200 g of liquid zinc amalgam, the liquid volume being adjusted to below 200 ml and the concentration of sulfuric acid to 1 N. Carbon dioxide was passed through the vessel to substitute the air, the vessel was shaken vigorously for 4~5 minutes to reduce quadrivalent titanium to trivalent state completely, and then the liquid zinc amalgam was removed. This solution was titrated with 0.1N

ferric ammonium sulfate using 10 ml of 40 per cent potassium thiocyanate solution as the indicator, until a persistent pale pink color was obtained. The total amount of titanium was calculated from the following equation:

$$\text{Ti}\% = \frac{\text{Titre of 0.1N Fe}(NH_4)(SO_4)_2\text{(ml)} \times 0.479}{\text{Sample (g)}}$$

4. Determination of total aluminium

The sample, 0.5~1 g, was placed in a beaker containing 50 ml of 2 N hydrochloric acid, 5 ml of 6 N nitric acid was added to oxidize titanium and the mixture was boiled for a few minutes. To this, 10 ml of 10 per cent disodium hydrogen phosphate was added, the excess acid was neutralized with 6 N sodium hydroxide but the alkali was not enough to cause precipitation, and this solution was poured gradually into a hot mixture of 10 ml of 10 per cent disodium hydrogen phosphate and 70 ml of 20 per cent sodium hydroxide with stirring to precipitate titanium. After boiling for a few minutes, the cooled mixture was transferred to a 250 ml measuring flask, the total volume was brought to 250 ml with water, shaken thoroughly, and allowed to stand. When the precipitate was settled, it was filtered through a dry filter, the initial filtrate was discarded, and the following 25 ml was collected. The filtrate thus collected was rendered weakly acid with 6 N hydrochloric acid, each 2 g of tartaric acid and ammonium chloride were added, and neutralized with ammonium hydroxide and its pH was adjusted to 9. Then it was warmed at 70°C, and a slight excess of glacial acetic acid solution of 3 per cent 8-hydroxyquinoline was added to precipitate aluminium. Ammonium hydroxide was then added torestore pH to the original, warming was continued to settle the precipitate, and the precipitate was collected in a sintered glass filter. The precipitate on the filter was washed thoroughly with warm water.

The precipitate was dried at 110°C, cooled and weighed as $Al(C_9H_6ON)_3$. The amount of Al was calculated from the following equation:

$$\text{Al}\% = \frac{Al(C_9H_6ON)_3\text{ (g)} \times 5.87 \times 10}{\text{Sample (g)}}$$

5. Determination of metallic aluminium

It is possible to separately determine metallic aluminium, because when the sample is treated with water, the chlorides of titanium and aluminium dissolve easily but metallic alone remains as an insoluble residue.

Procedure 1 (Gravimetric method): The sample, 1~2 g was dissolved with agitation into 100 ml of water contained in a beaker. The insoluble metallic aluminium was collected immediately by filtration with suction through a Gooch crucible containing asbestos or sintered glass filter and the residue was washed thoroughly with water, discarding the filtrate. The residue on the filter was dissolved by pouring a hot mixture of 20 ml of 6N hydrochloric acid and 5 ml of 6N nitric acid, while pulling gently through suction, and the filter was washed thoroughly with hot hydrochloric acid (1 : 100).

The combined solution and washings were used as the sample, approximately

neutralized with 6N sodium hydroxide solution, and poured into 70 ml of 20 per cent sodium hydroxide solution. The amount of aluminium was gravimetrically determined as for the determination of total aluminium.

Procedure 2 (Volumetric method): The insoluble residue obtained by treatment with water, was washed thoroughly with water, then washed once with 1 per cent hydrogen peroxide solution containing 1 drop of sulfuric acid in order to remove trivalent titanium completely, and again washed with water to remove hydrogen peroxide.

The residue and the asbestos were removed from the crucible, transferred to an Erlenmeyer flask containing 3 g of ferric ammonium sulfate and 50 ml of 3N sulfuric acid and dissolved by warming in carbon dioxide stream. The mixture was then cooled with water and ferrous ion formed by reduction with metallic aluminium was titrated with 0.1N potassium permanganate solution, the end point being a pale pink color which persisted for 1 min. The amount of metallic aluminium was calculated from the following equation:

$$\text{Metallic Al}\% = \frac{\text{Titre of 0.1N } KMnO_4 \times 0.0899}{\text{Sample (g)}}$$

Procedure 3: Only in the case of a mixture of trivalent and quadrivalent titanium, titre of 0.1N potassium permanganate by dissolution in ferric salt solution (used sample of A″ g) and that of 0.1N ferric ammonium sulfate by dissolution in water (used sample of B″ g) were obtained, and the amount of metallic aluminium was calculated from the following equation:

$$\text{Metallic Al}\% = \left(\frac{\text{Titre of 0.1N } KMnO_4\text{(ml)}}{\text{Sample A}'' \text{ (g)}} - \frac{\text{Titre of 0.1N } Fe(NH_4)(SO_4)_2\text{ (ml)}}{\text{Sample B}'' \text{ (g)}}\right) \times 0.0899$$

6. Determination of total chlorine

Procedure: The sample, 0.5~1 g, was cautiously dissolved in 50 ml of water, 20 ml of 6N nitric acid was gradually added to oxidize trivalent to quadrivalent titanium, and gently heated until a clear solution resulted. Since metallic alminium often remained as an insoluble residue at this stage, the cooled solution was filtered into a 250 ml measuring flask, the residue and the filter were washed with nitric acid (1 : 100), and the total volume was brought to 250 ml with water.

10 or 25 ml portion of this solution was placed in a beaker, 5 ml of 6N nitric acid was added to prevent hydrolysis of titanium, and the total volume was made to 50 ml with water and then 0.2 N silver nitrate was added in slightly excess under stirring to precipitate silver chloride, and the stirring was continued until the precipitate gathered and settled. The precipitate was allowed to stand over night in a dark place, collected on a sintered glass filter, washed thoroughly with nitric acid (1 : 100), and finally washed once with water. After drying the precipitate at 130°C for 1 hour, the precipitate was cooled, weighed and the amount of chlorine was calculated from the following equation:

$$\text{Cl}\% = \frac{\text{AgCl (g)} \times 24.74 \times (25 \text{ or } 10)}{\text{Sample (g)}}$$

III. Experimental results

The results of the determinations of total titanium, bivalent and trivalent titanium, total aluminium, metallic aluminium, and total chlorine, from a mixture of bivalent and trivalent titanium and a mixture of trivalent and quadrivalent titanium are listed in Tables 1 and 2. As seen from these tables, well-agreeing values were obtained for the amount of bivalent titanium by the methods of dissolution in ferric salt solution and in water and by dissolution in ferric salt solution and from total titanium and for the amount of trivalent titanium by the method of dissolution in ferric salt solution corrected for the titre for metallic aluminium and that determined from the filtrate of dissolution in water.

Table 1. Results of the chemical analysis of the mixture of Ti^{2+} and Ti^{3+}.

Constituent	Total Ti (%)	Ti^{2+} (%)		Ti^{3+} (%)		Total Al (%)	Metallic Al (%)	Total Cl (%)	Total (%)
Sample No.		A method	B method	A method	B method		Gravimetric method		Total Ti + Total Al + Total Cl
487	24.38	1.09	0.90	23.10	23.48	13.69	3.16	60.66	98.73
493	29.46	—	3.80	—	25.66	5.32	0.76	61.62	96.40
603	32.28	3.08	3.13	29.24	29.15	7.98	0.94	57.35	97.61
604	34.14	—	11.18	—	22.96	6.22	0.87	54.15	94.51

1) Method A was the procedure (B′) described in part (ii) of section II–2.
2) Method B was the procedure (A′) destribed in part (ii) of section II–2.

Table 2. Results of chemical analysis of the mixture of Ti^{3+} and Ti^{4+}.

Constituent / Sample No.	Total Ti (%)	Ti^{3+} (%)		Ti^{4+} (%)	Total Al (%)	Metallic Al (%)			Total Cl (%)	Total (%)
		A method	B method	Total Ti–Ti^{3+}		Gravimetric method	Volumetric method	Subtracting method		Total Ti + Total Al + Total Cl
413	18.83	—	18.83	—	8.44	0.00	—	—	71.15	98.42
510	21.16	11.56	—	9.60	5.16	0.80	—	—	71.42	97.74
521	25.08	18.92	—	6.16	6.35	1.25	—	—	66.04	97.47
531	26.83	26.57	26.46	0.32	6.65	0.94	—	0.92	62.42	95.90
571	23.27	15.64	15.23	7.83	5.68	0.57	—	0.49	70.34	99.29
573	21.31	16.18	17.00	4.72	10.01	1.35	—	1.51	64.55	95.87
574	27.40	26.36	26.24	1.10	7.37	1.28	—	1.26	63.42	98.19
668	22.76	13.35	13.67	9.25	4.90	0.56	—	0.62	71.00	98.66
729	21.98	10.15	10.39	11.71	4.72	—	0.56	0.61	71.81	98.51
747	23.45	9.16	9.01	14.37	3.70	—	0.17	0.15	71.93	99.08
765	21.54	10.99	10.96	10.56	7.68	—	0.44	0.43	70.06	99.28
778	22.81	11.74	11.69	11.09	4.43	0.42	0.38	0.39	71.67	98.91
779	22.81	10.75	10.64	12.11	3.96	0.36	0.36	0.34	71.77	98.54
799	21.49	12.57	12.95	8.73	5.93	0.59	—	0.66	71.12	98.54
835	22.93	18.70	18.34	4.41	7.80	1.17	1.22	1.12	68.01	98.72

1) Method A was the procedure (A) described in part (i) of section II–2.
2) Method B was the procedure (B) described in part (ii) of section II–2.

In the determination of metallic aluminium by gravimetric and volumetric methods from the residue obtained after dissolution in water, it had been assumed that the values would be varied due to the variation of pH by the hydrochloric acid formed by decomposition of the chlorides and causing dissolution of some

metallic aluminium. However, the values obtained agreed with the amount of metallic aluminium calculated by the difference of titre in the methods of dissolving in ferric salt solution and in water. It was thereby observed that there was practically no loss of metallic aluminium by dissolution due to different pH of the solution.

In the sample, bivalent, trivalent and quadrivalent titanium, and aluminium other than metallic aluminium are assumed to be present as titanium dichloride, trichloride, tetrachloride and aluminium trichloride. When a large amount of oxidizable bivalent or trivalent titanium are present, the sum of the amount of total titanium, total aluminium and total chlorine comes within 95~98per cent. When the amount of titanium dichloride, trichloride and aluminium trichloride calculated from the amount of bivalent and trivalent titanium and aluminium in (total aluminium − metallic aluminium), the sum of the amount of chlorine becomes much greater than that obtained by the actual determination. It is true that it is difficult to obtain a uniform portion of the sample because of its liability to undergo decomposition, but, since the determined values for bivalent, trivalent titanium and metallic aluminium by various method agree well and since it seems impossible to allow for more than 1~2 per cent of error from total titamium, total chlorine and total aluminium, the reason for the discrepancy of the amount of total chlorine is probably due to the formation of oxychlorides by oxidation, such as TiOCl, $TiOCl_2$, $Ti(OH)Cl_2$, and $Ti(OH)Cl_3$, and other complex oxidation products.

On the contrary, when the amount of trivalent and quadrivalent titanium is close, the total sum is 98~99 per cent, indicating more difficulty of oxidation than in the case of the presence of a large amount of bivalent or trivalent titanium. It is assumed, therefore, that the majority of trivalent and quadrivalent titanium are present as titanium trichloride, and titanium tetrachloride, with a slight occlusion of oxychlorides.

It is almost impossible to determine the amount of oxygen and oxychlorides thought to be present in the sample by separatory determination at the present stage and therefore, it is difficult to make reliable prediction of these compositions.

Summary

(1) The amount of low valency bivalent and trivalent titanium contained in the reduced compounds of titanium chloride was calculated from the titre of potassium permanganate solution for acidic ferric salt decomposition and that of ferric salt solution for the filtrate obtained on dissolution in water or that of ferric salt solution for total titanium.

(2) The total amount of aluminium was determined by the oxine method and the total chlorine was determined by gravimetric method as silver chloride by the use of silver nitrate solution.

(3) The amount of metallic aluminium was determined by the gravimetric or volumetric method from the residue obtained by decomposition of the sample with water. When the sample did not contain bivalent titanium, the amount of metallic

aluminium was easily calculated from the difference between the titre of potassium permanganate for dissolution in acidic ferric salt solution and it of ferric salt solution for dissolution in water. The values by these three methods agreed well.
(4) The foregoing experiments have definitely established the method of determining the amounts of bivalent, trivalent titanium, total aluminium, metallic aluminium and total chlorine present in the reduced compounds of titanium chloride.